



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) EP 1 072 599 A1

# EUROPEAN PATENT APPLICATION

(12)

(43) Date of publication:  
31.01.2001 Bulletin 2001/05

(51) Int. Cl.<sup>7</sup>: C07D 301/12

(21) Application number: 00202657.3

(22) Date of filing: 24.07.2000

(84) Designated Contracting States:  
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE  
Designated Extension States:  
AL LT LV MK RO SI

(30) Priority: 27.07.1999 IT MI991657

(71) Applicant: Enichem S.p.A.  
20097 S. Donato Milanese (Milano) (IT)

(72) Inventors:

- Paparatto, Giuseppe  
20092 Cinisello Balsamo, Milan (IT)
- Forlin, Anna  
35010 Vigonza, Padova (IT)
- Tregon, Paolo  
30030 Oriago, Venezia (IT)

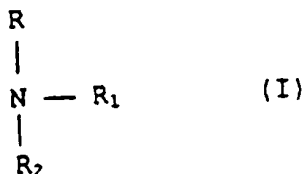
(74) Representative:

De Gregori, Antonella  
Ing. Barzano & Zanardo Milano S.p.A.  
Via Borgonuovo 10  
20121 Milano (IT)

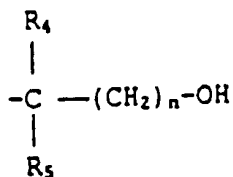
(54) Process for the preparation of olefin oxides

(57) A process in continuous is described for the preparation of oxides of olefins by the direct epoxidation of an olefin with hydrogen peroxide, or compounds capable of producing hydrogen peroxide under the reaction conditions, in a solvent medium, in the presence of a catalytic system consisting of a zeolite containing titanium and a nitrogenated organic base having formula (I).

group, wherein n is a number ranging from 1 to 10 and R<sub>4</sub> and R<sub>5</sub> are H or an alkyl group with C<sub>1</sub>-C<sub>10</sub> carbon atoms, on the condition that R, R<sub>1</sub> and R<sub>2</sub> are not contemporaneously H.



wherein: R, R<sub>1</sub>, and R<sub>2</sub>, the same or different, can be H, an alkyl group with C<sub>1</sub>-C<sub>10</sub> carbon atoms, a -COR<sub>3</sub> group wherein R<sub>3</sub> is an alkyl group with C<sub>1</sub>-C<sub>10</sub> carbon atoms, or a



EP 1 072 599 A1

## Description

[0001] The present invention relates to a process in continuous for the preparation of olefin oxides.

[0002] More specifically, the present invention relates to a process in continuous for the preparation of propylene oxide by the direct epoxidation of propylene with hydrogen peroxide, or compounds capable of producing hydrogen peroxide under the reaction conditions, in a solvent medium, in the presence of a catalytic system consisting of a zeolite containing titanium and a nitrogenated organic base having formula (I).

[0003] Epoxides, or olefin oxides, are intermediates useful for the preparation of a wide variety of compounds. For example epoxides can be used for the production of glycols, condensation polymers such as polyesters, or for the preparation of intermediates useful in the synthesis of polyurethane foams, elastomers, seals and similar products.

[0004] It is known in literature that zeolitic compounds with an MFI structure containing titanium atoms (TS-1) are used as catalysts in the direct epoxidation reactions of olefin compounds with hydrogen peroxide (EP-100119).

[0005] However, the acidity which characterizes these catalysts, even if modest, is sufficient to catalyze consecutive solvolytic reactions on the epoxide with the opening of the ring. This leads to an increase in production costs for both the decrease in yield to epoxide and for the separation of the by-products formed.

[0006] To overcome these disadvantages, processes have been proposed in the art for improving the catalytic performances of these zeolitic compounds by appropriate activation treatment.

[0007] For example, the patent U.S. 4,937,216 describes a process for the preparation of epoxides from olefins and hydrogen peroxide which uses, as catalyst, a titanium silicalite treated, before or during the epoxidation reaction, with a neutralizing agent selected from organic derivatives of silicon of the type X-Si(R)<sub>3</sub> or hydrosoluble substances deriving from cations of group I and II with a different base strength.

[0008] The patent EP-712.852 discloses an epoxidation process of olefins in the presence of titanium-silicalite which uses as neutralizing agent a non base salt selected from lithium chloride, sodium nitrate, potassium sulfate and ammonium phosphate.

[0009] The patent U.S. 5,675,026 describes an epoxidation process which uses as catalyst a titanium-silicalite treated, before or during the reaction, with a neutral salt or acid, selected from Na<sub>2</sub>SO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>NO<sub>3</sub> or NaH<sub>2</sub>PO<sub>4</sub>.

[0010] Operating according to these known processes, propylene oxide is obtained with a good yield and selectivity.

[0011] These processes however have disadvantages deriving from the fact that these catalytic systems have a short duration of the catalytic cycle and consequently require frequent regeneration.

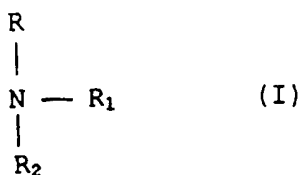
[0012] This creates considerable problems from both a technical and economic point of view, above all when the epoxidation process is carried out in continuous.

[0013] In fact, a lowering in the production yield of the epoxide and a reduction of the catalytic activity have been observed during the subsequent regeneration phases.

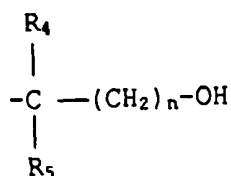
[0014] There is therefore the obvious necessity of developing epoxidation processes which allow a high conversion and selectivity to be obtained, simultaneously maintaining the stability of the catalytic activity during the reaction.

[0015] It has now been found that these requirements can be satisfied if the epoxidation reaction of olefins is carried out in the presence of suitable nitrogenated bases.

[0016] In accordance with this, the present invention relates to a process in continuous for the preparation of olefin oxides by the direct oxidation of an olefin with hydrogen peroxide, or compounds capable of producing hydrogen peroxide under the reaction conditions, in a solvent medium, in the presence of a catalytic system consisting of a synthetic zeolite containing titanium atoms and a nitrogenated base having general formula (I)



wherein: R, R<sub>1</sub> and R<sub>2</sub>, the same or different, can be H, an alkyl group with C<sub>1</sub>-C<sub>10</sub> carbon atoms, a -COR<sub>3</sub> group wherein R<sub>3</sub> is an alkyl group with C<sub>1</sub>-C<sub>10</sub> carbon atoms, or a



group wherein n is a number ranging from 1 to 10 and  $R_4$  and  $R_5$  are H or an alkyl group with  $C_1$ - $C_{10}$  carbon atoms, on the condition that  $R$ ,  $R_1$  and  $R_2$  are not contemporaneously H.

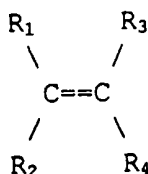
[0017] Preferred compounds having formula (I) are: methylamine, ethylamine, n-propylamine, diethylamine, n-butylamine, ethanolamine, diethanolamine, triethanolamine and urea.

[0018] The compound having formula (I) is fed in continuous and is present in such a concentration as to neutralize the acidity of the reaction mixture.

[0019] The concentration however of this compound (I) generally ranges from 5 to 500 ppm (by weight) with respect to the reaction mixture, preferably from 10 to 100 ppm.

[0020] The olefin compounds which can be used in the process of the present invention can be selected from organic compounds having at least one double bond and can be aromatic, aliphatic, alkylaromatic, cyclic, branched or linear. They are preferably olefin hydrocarbons having from 2 to 30 carbon atoms in the molecule and containing at least one double bond.

[0021] Examples of olefins suitable for the purposes of the present invention are selected from those having general formula (II)



wherein:  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$ , the same or different, can be H, an alkyl radical with from 1 to 20 carbon atoms, an aryl radical, an alkylaryl radical with from 7 to 20 carbon atoms, a cycloalkyl radical with from 6 to 10 carbon atoms, an alkylcycloalkyl radical with from 7 to 20 carbon atoms. The radicals  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$ , can form, in pairs, saturated or unsaturated rings. These radicals may additionally contain halogen atoms, nitro, nitrile, sulfonic groups and relative esters, carbonyl, hydroxyl, carboxyl, thiol, amine and ether groups.

[0022] Examples of olefins which can be epoxidated with the process of the present invention are: ethylene, propylene, allyl chloride, allyl alcohol, butenes, pentenes, hexenes, octeneheptenes-1, 1-tridecene, mesityl oxide, isoprene, cyclo-octene, cyclohexene or bicyclic compounds such as norbornenes, pinenes, etc.

[0023] The olefins can carry the above substituents both on the unsaturated carbon atoms and on different positions.

[0024] The oxidizing agent used in the process of the present invention is hydrogen peroxide ( $H_2O_2$ ) or a compound which is capable of generating  $H_2O_2$  under the epoxidation conditions.

[0025] An aqueous solution of hydrogen peroxide is preferably used, at a minimum concentration of 1% by weight, preferably with a titer greater than or equal to 35% by weight.

[0026] The quantity of hydrogen peroxide with respect to the olefin is not critical, but a molar ratio olefin/ $H_2O_2$  ranging from 10:1 to 1:10, preferably from 6:1 to 1:2, is preferably used.

[0027] The epoxidation reaction can be carried out in one or more solvents liquid at the epoxidation temperatures. Solvents of a polar nature are typically used, such as alcohols (methanol, ethanol, isopropyl alcohol, t-butyl alcohol, cyclohexanol), ketones (for example acetone, methyl ethyl ketone, acetophenone), ethers (tetrahydrofuran, butyl ether), aliphatic and aromatic hydrocarbons, halogenated hydrocarbons, esters.

[0028] Methanol and, among the ketones, acetone, are preferably used. A mixture of methanol/water with a weight ratio ranging from 50/50 to 99/1, is particularly preferred.

[0029] The temperatures used in the process of the present invention generally range from 20 to 150°C, preferably from 40 to 100°C. The operating pressures are those which allow the olefin to be maintained in liquid phase at the pre-

set reaction temperature. The operating pressure is generally higher than atmospheric pressure when gaseous olefins are used.

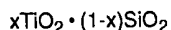
[0030] The catalyst which can be used in the process of the present invention is selected from those generally known by the name of titanium-silicalites.

[0031] For example titanium-silicalites with an MFI structure can be used, described in the patent U.S. 4,410,501 which also specifies their structural characteristics.

[0032] Titanium-silicalites can also be used, in which part of the titanium is substituted by other metals, such as boron, aluminum, iron or gallium. These substituted titanium silicalites and the methods for their preparation are described in European patent applications 226,257, 226,258 and 266,825.

[0033] It is also possible to use titanium silicalites with a MEL or intermediate MFI/MEL structure described in Belgian patent 1,001,038. Other titanium-silicalites can be selected from beta zeolites containing titanium and having a BEA structure, described in Spanish patent 2,037,596, ZSM-12 containing titanium and optionally aluminum, described in "Journal of Chemical Communications, 1992, page 745).

[0034] The preferred catalyst according to the present invention is titanium-silicalite having the general formula:



wherein: x represents a number ranging from 0.0001 to 0.04, preferably from 0.01 to 0.025, and described, for example, in U.S. patents 4,410,501, 4,824,976, 4,666,692, 4,656,016, 4,859,785, 4,937,216.

[0035] The quantity of catalyst used in the process of the present invention is not critical; it is selected however in such a way as to allow the epoxidation reaction to be completed in as short a time as possible.

[0036] The quantity of catalyst is generally selected in relation to various parameters, such as the reaction temperature, the reactivity and concentration of the olefins, the concentration of hydrogen peroxide, the type and composition of the solvent, the catalytic activity and type of reactor or reaction system used.

[0037] The quantity of catalyst typically ranges from 1 to 15% by weight with respect to the reaction mixture and, preferably, from 4 to 10% by weight.

[0038] The catalyst can be used in the form of powder, pellets, microspheres, extruded product or other convenient physical forms.

[0039] The epoxidation process of the present invention can be carried out in batch, semi-continuous or, preferably, in continuous.

[0040] Various types of reactor can be used in the process of the present invention, for example a slurry reactor or a fixed-bed reactor.

[0041] The epoxidation process is preferably carried out in continuous, by feeding into a reaction zone containing the catalyst: the solvent, hydrogen peroxide, the olefin and the compound having general formula (I).

[0042] The epoxide obtained with the process of the present invention can be separated and recovered from the reaction mixture using suitable techniques such as fractionated distillation.

[0043] The following examples have the sole purpose of describing the present invention in greater detail and should in no way be considered as limiting its scope.

#### Example 1 (comparative)

##### Oxidation of propylene

[0044] The epoxidation reaction is carried out in a stirred, 1.5 litre, AISI 316L steel reactor, equipped with a thermostat-regulation system, level control, pressure control and filter for continuously removing the solution, maintaining the catalyst in the reactor.

[0045] 760 g of a solution of methanol/water (93/7) and 40 g of titanium silicalite TS-1 (EniChem, with a titanium content equal to 2.05% by weight) are initially charged.

[0046] After thermostat-regulating the system at 60°C and pressurizing with propylene to 12 bar, the following products are fed in continuous by means of pumps:

1. 1970 g/hour of a solution of methanol/water 92.8/7.2 by weight
2. 230 g/hour of an aqueous solution of H<sub>2</sub>O<sub>2</sub> at 35% by weight
3. propylene
4. 100 g/hour of water.

[0047] The overall reaction mixture in the feeding (without propylene) is equal to 2300 g/hour and its composition is the following:

H<sub>2</sub>O<sub>2</sub> 3.5%, H<sub>2</sub>O 17%, MeOH 79.5%.

The pressure in the reactor is maintained at 12 bar, feeding propylene.

[0048] The reaction trend is followed by taking samples every two hours and determining the residual H<sub>2</sub>O<sub>2</sub> by titration with sodium thiosulfate and the reaction products by gaschromatography.

5 [0049] The results are indicated in Table 1.

Table 1

Reaction hours	H <sub>2</sub> O <sub>2</sub> conversion %	PO selectivity %
6	90	67
16	82	75
30	75	80

10

15

#### Example 2 (comparative)

[0050] The reaction is carried out under the same conditions described in example 1, but feeding in continuous (100 g/hour) an aqueous solution containing 0.115% by weight of sodium acetate, corresponding to 50 ppm of the reaction mixture. The results are indicated in table 2.

20

Table 2

Reaction hours	H <sub>2</sub> O <sub>2</sub> conversion %	PO selectivity %
6	96	84
16	94	91
30	87	96

25

30

#### Example 3 (comparative)

[0051] The same procedure is adopted as in example 1, but feeding in continuous (100 g/hour) an aqueous solution containing 0.092% by weight of NaNO<sub>3</sub>, corresponding to 40 ppm in the reaction mixture. The results are shown in table 3.

35

Table 3

Reaction hours	H <sub>2</sub> O <sub>2</sub> conversion %	PO selectivity %
6	92	71
16	87	82
30	84	86

40

45

#### Example 4 (comparative)

[0052] The same procedure is adopted as in example 1, but feeding in continuous (100 g/hour) an aqueous solution containing 0.046% by weight of NaOH, corresponding to 20 ppm in the reaction mixture. The results are shown in table 4.

50

Table 4

Reaction hours	H <sub>2</sub> O <sub>2</sub> conversion %	PO selectivity %
6	85	93
16	65	97.5

55

# EP 1 072 599 A1

Table 4 (continued)

Reaction hours	H <sub>2</sub> O <sub>2</sub> conversion %	PO selectivity %
30	45	98

## Example 5

[0053] The same procedure is adopted as in example 1, but feeding (100 g/hour) an aqueous solution containing 0.23% of ethanolamine, corresponding to 100 ppm in the reaction mixture. The results are shown in table 5.

Table 5

Reaction hours	H <sub>2</sub> O <sub>2</sub> conversion %	PO selectivity %
6	94	97.5
30	92.5	97.2
40	89	97.4

## Example 6

[0054] The same procedure is adopted as in example 1, but feeding (100 g/hour) an aqueous solution containing 0.23% of ethylamine, corresponding to 100 ppm in the reaction mixture. The results are shown in table 6.

Table 6

Reaction hours	H <sub>2</sub> O <sub>2</sub> conversion %	PO selectivity %
6	95	96.8
30	92	96.5
40	91	97.5

## Example 7

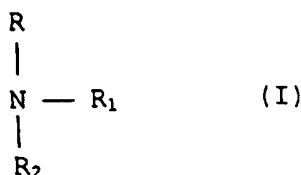
[0055] The same procedure is adopted as in example 1, but feeding (100 g/hour) an aqueous solution containing 0.23% of n-propylamine, corresponding to 100 ppm in the reaction mixture. The results are shown in table 7.

Table 7

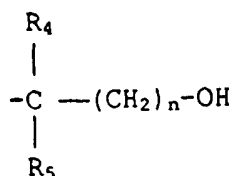
Reaction hours	H <sub>2</sub> O <sub>2</sub> conversion %	PO selectivity %
6	92	96.5
30	91.5	96.8
40	91.7	97

## Claims

1. A process in continuous for the preparation of olefin oxides by the direct epoxidation of an olefin with hydrogen peroxide, or compounds capable of producing hydrogen peroxide under the reaction conditions, in a solvent medium, in the presence of a catalytic system consisting of a zeolite containing titanium atoms and a nitrogenated base having general formula (I)

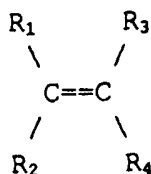


wherein: R, R<sub>1</sub> and R<sub>2</sub>, the same or different, can be H, an alkyl group with C<sub>1</sub>-C<sub>10</sub> carbon atoms, a -COR<sub>3</sub> group wherein R<sub>3</sub> is an alkyl group with C<sub>1</sub>-C<sub>10</sub> carbon atoms, or a



group, wherein n is a number ranging from 1 to 10 and R<sub>4</sub> and R<sub>5</sub> are H or an alkyl group with C<sub>1</sub>-C<sub>10</sub> carbon atoms, on the condition that R, R<sub>1</sub> and R<sub>2</sub> are not contemporaneously H.

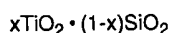
2. The process according to claim 1, wherein the compound having formula (I) is selected from ethylamine, n-propylamine, diethylamine, n-butylamine, ethanolamine, diethanolamine and triethanolamine.
3. The process according to claim 1, wherein the starting olefin compounds are selected from aromatic, aliphatic, alkylaromatic, cyclic, branched or linear organic compounds, having at least one double bond.
4. The process according to claim 3, wherein the olefin compounds are selected from olefin hydrocarbons having from 2 to 30 carbon atoms in the molecule and containing at least one double bond.
5. The process according to claim 4, wherein the olefin compounds are selected from those having general formula (II)



wherein: R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub>, the same or different, can be H, an alkyl radical with from 1 to 20 carbon atoms, an aryl radical, an alkylaryl radical with from 7 to 20 carbon atoms, a cycloalkyl radical with from 6 to 10 carbon atoms, an alkylcycloalkyl radical with from 7 to 20 carbon atoms.

6. The process according to claim 5, wherein the radicals R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> can form, in pairs, saturated or unsaturated rings.
7. The process according to claim 4, wherein the radicals R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> can contain substituents selected from halogens, nitro, nitrile, sulfonic groups and relative esters, carbonyl, hydroxyl, carboxyl, thiol amine and ether groups.

8. The process according to claim 1, wherein the olefin is propylene.
9. The process according to claim 1, wherein the compound having formula (I) is used in a quantity ranging from 5 to 500 ppm by weight with respect to the reaction mixture.
- 5 10. The process according to claim 9, wherein the compound having formula (I) is used in a quantity ranging from 10 to 100 ppm by weight with respect to the reaction mixture.
11. The process according to claim 1, wherein the hydrogen peroxide is used as an aqueous solution with a minimum  
10 titer of 1% by weight.
12. The process according to claim 11, wherein the hydrogen peroxide is used as an aqueous solution with a titer equal to or higher than 35% by weight.
- 15 13. The process according claim 1, wherein the molar ratio between olefin and hydrogen peroxide ranges from 10/1 to 1/10.
14. The process according claim 13, wherein the molar ratio between olefin and hydrogen peroxide ranges from 6/1 to 1/2.
- 20 15. The process according to claim 1, wherein the catalyst is selected from titanium silicalites having the following general formula:



25 wherein: x ranges from 0.0001 to 0.04.

16. The process according to claim 15, wherein the value of x ranges from 0.01 to 0.025
- 30 17. The process according to claim 15, wherein in the titanium silicalite part of the titanium is substituted by metals selected from boron, aluminum, iron or gallium.
18. The process according to claim 1, wherein the epoxidation reaction is carried out in one or more solvents, liquid at the epoxidation temperatures, selected from alcohols, ketones, ethers, aliphatic and aromatic hydrocarbons, halo-  
35 genated hydrocarbons, esters and glycols.
19. The process according to claim 18, wherein the alcohols are selected from methanol, ethanol, isopropyl alcohol, t-butyl alcohol, cyclohexanol.
- 40 20. The process according to claim 18, wherein the ketones are selected from acetone, methyl ethyl ketone, acetophenone.
21. The process according to claim 18, wherein the ethers are selected from tetrahydrofuran and butyl ether.
- 45 22. The process according to claim 18, wherein the solvent medium is a mixture of methanol/water with a weight ratio ranging from 50/50 and 99/1.
23. The process according to claim 1, wherein the epoxidation reaction is carried out at a temperature ranging from 20 to 150°C.
- 50 24. The process according to claim 21, wherein the temperature ranges from 40 to 100°C.



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 00 20 2657

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
D,X	EP 0 230 949 A (ENIRICERCH S.P.A. ET AL) 5 August 1987 (1987-08-05) * the whole document, particularly claims 3 and 7 *	1-24	C07D301/12
D,A	EP 0 757 043 A (DEGUSSA AKTIENGESELLSCHAFT) 5 February 1997 (1997-02-05) * the whole document *	1	
P,X	EP 0 940 393 A (ENICHEM S.P.A.) 8 September 1999 (1999-09-08) * the whole document *	1,3-24	
P,X	WO 00 17178 A (ARCO CHEMICAL TECHNOLOGY L.P. ET AL) 30 March 2000 (2000-03-30) * the whole document *	1-24	
P,X	DATABASE WPI Section Ch, Week 200007 Derwent Publications Ltd., London, GB; Class E13, AN 2000-075359 XP002151674 & JP 11 309378 A (ASAHI KASEI KOGYO KK ET AL), 9 November 1999 (1999-11-09) * abstract *	1-24	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C07D
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		1 November 2000	Allard, M
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 03/82 (P4/C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 20 2657

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

01-11-2000

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 230949	A	05-08-1987	IT 1190605 B	16-02-1988
			IT 1190606 B	16-02-1988
			AT 78475 T	15-08-1992
			DE 3780476 A	27-08-1992
			DE 3780476 T	17-12-1992
			ES 2033693 T	01-04-1993
			GR 3005253 T	24-05-1993
			JP 2118264 C	06-12-1996
			JP 8016105 B	21-02-1996
			JP 62185081 A	13-08-1987
			US 4824976 A	25-04-1989
			US 4937216 A	26-06-1990
EP 757043	A	05-02-1997	DE 19528219 A	06-02-1997
			BR 9603245 A	28-04-1998
			CA 2182436 A	02-02-1997
			CN 1147510 A	16-04-1997
			JP 9118671 A	06-05-1997
			KR 189031 B	01-06-1999
			SG 42428 A	15-08-1997
			US 5675026 A	07-10-1997
EP 940393	A	08-09-1999	IT MI980441 A	06-09-1999
			US 6060610 A	09-05-2000
WO 0017178	A	30-03-2000	US 6037484 A	14-03-2000
			AU 6193299 A	10-04-2000
JP 11309378	A	09-11-1999	NONE	

EPO FORM P4489

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82